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THE RADIOACTIVE ISOTOPE OF HYDROGEN (TRITIUM) AND ITS USE AS AN INDICATOR OF CHEMICAL REACTIONS

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Moscow
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/Numbers in parentheses refer to the bibliography at the end./

The hydrogen isotope with a mass of 3, called tritium, has become well known in recent years as one of the artificially radioactive elements. In view of the fact that this isotope is more difficult to obtain than deuterium, it has not yet been studied as much, but its properties show great promise for studying the mechanism of various processes by the radioactive indicator method.

Artificial atomic fission was first accomplished by Rutherford (1) in 1919. By bombarding nitrogen with alpha particles, he obtained a stable oxygen isotope: ${}_7N^{14} + {}_2He^4 \rightarrow {}_8O^{16} + {}_1H^1$. Artificial radioactivity -- i.e., producing an unstable, disintegrating element -- was accomplished only 15 years later by F. Joliot and I. Curie (2) with the action of alpha particles of polonium on aluminum and boron:

$$ {}^{27}_{13}Al + {}^{4}_{2}He \longrightarrow {}^{30}_{15}P + {}^{1}_{0}n ; $$

$$ {}^{10}_{5}B + {}^{4}_{2}He \longrightarrow {}^{13}_{7}N + {}^{1}_{0}n . $$

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As a result of these nuclear reactions, unstable isotopes of phosphorus and nitrogen are formed, which disintegrate further in a manner analogous to natural radioactive elements, forming carbon and sulphur isotopes:

$${}^{30}_{15}P \longrightarrow {}^{30}_{14}S + \overset{+}{e} \qquad \text{(half life -- approximately 3 min)}$$

$${}^{13}_{7}N \longrightarrow {}^{13}_{6}C + \overset{+}{e} \qquad \text{(half life -- approximately 14 min)}$$

From this time, the number of discovered nuclear reactions which led to the production of artificial radioactive elements began to increase rapidly. However, further progress was complicated by the fact that the particles used for bombarding nuclei have their own charge which inhibits the penetration of these particles into heavy atoms. The idea of using particles without a charge and therefore capable of penetrating any atom and destroying its nucleus was suggested in 1920 by Rutherford (3). This idea was realized in 1934 by Fermi and his colleagues (4) who used neutrons for this purpose. Radon tubes containing a mixture of radium with beryllium powder ${}_4Be^{9}(an)\,{}_4Be^{10}$ served as a source of neutrons. In his first publication, Fermi described the formation of more than 40 radioactive elements obtained by bombarding various elements with neutrons. Since then, artificial production of elements has been widely developed, and at the present time the atoms of a majority of chemical substances have been split, so that the number of artificially radioactive elements exceeds 300. This has made possible wide use of radioactive elements for studying various processes in different fields of chemistry, biology, and medicine by the method of radioactive indicators ("tracer" atoms).

The use of natural radioactive substances as indicators was begun in the works of Hevesy and Panneth (5) and others, and in the USSR in the works of V. G. Khlopin (6). Since 1935, artificial radioactive elements have been used for this purpose by Juliusburger, Tople and Hess (7), Erbacher and Phillip (8), and in the USSR by S. Z. Roginskiy and his colleagues (9).

The radioactive indicator method makes it possible to observe the conduct of any minute quantity of a substance which would be impossible to detect by any other physical or chemical methods (quantities on the order of 10^{-12} to 10^{-16} moles, depending upon the length of the half life). In addition, this method permits the realization of rapid and almost constant control of the location of "tracer" molecules, regardless of the presence of any other substances and complications of the system; it also makes it possible to study exchange processes. All of these advantages of the radioactive indicator method have attracted a large number of investigators to it (see, for example, items 10-13 in the bibliography).

Recently, the radioactive hydrogen isotope, tritium, has been used to explain the mechanism of a large number of processes connected with the migration of the hydrogen atom. The discovery of deuterium (11) in 1932, and the production of pure heavy water (15) in 1933, gave an intense impetus to the study of such processes by using "tracer" atoms of deuterium, but analytical and other possibilities offered by the use of tritium are considerably greater. Unfortunately, the weak radioactivity of tritium (the energy of the beta particle is approximately 0.015 MeV) and the fact that it is still not easily obtainable considerably limits the wider use of this isotope.

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I. THE DISCOVERY OF TRITIUM

In 1934, Rutherford and his colleagues (16) studied the nuclear process by bombarding deuterium with deuterons with an energy of 20,000 to 100,000 eV. Deuterio-ammonium salts, ND_4Cl, $(ND_4)_2SO_4$ and D_3PO_4, were used as targets. The emission of two groups of single-charged particles was noticed, one with a flight through the air of approximately 14.3 cm, and the other 1.6 cm. The number of particles of both types appeared to be equal. Consideration of these results led the authors to the conclusion that the particles with the shortest flight are nuclei of a new hydrogen isotope with a mass of 3.0151, formed as a result of nuclear transformation: ${}_1D^2 + {}_1D^2 \longrightarrow {}_1H^3 + {}_1H^1$. The number of radiated particles was established as a function of the energy of the accelerated nuclei of deuterium; and with 100,000 eV, 10^6 deuterons hitting the target formed one atom of tritium. In the second work of these authors (17), the length of flight of the particles was determined more precisely and the energy of the specified nuclear γ-transformation was calculated as 3.97 ± 0.02 MeV. The mass of tritium was determined exactly as 3.0152 ± 0.0002. Soon Fermi (3) and Chadwick and Goldhaber (18) independently discovered a new hydrogen isotope by bombardment of lithium atoms with neutrons:

$$ {}_3Li^6 + {}_0n^1 \longrightarrow {}_2He^4 + {}_1H^3. $$

Study of almost pure deuterium with the mass spectrograph by Tuve and his colleauges (19), and Lozier and others (20) indicated the presence of a hydrogen isotope with a mass of 3. At that time it seemed that this must be an energetically stable isotope (13) which would be found in nature, although in very small quantities. In order to determine its presence in ordinary water, Rutherford (21) tried to separate it in 1937. Eleven cubic centimeters of heavy water were obtained in Norway by electrolysis of 13,000 tons of water, i.e., the volume was reduced 10^9 times. However, lines corresponding to an ion $(DT)^+$ were not discovered on a very exact Aston mass spectrograph. Therefore Rutherford came to the conclusion that the H^3 isotope, apparently, is unstable, which explains its negligible quantity in nature. Bonner (22) came to the same conclusion on the basis of his own calculations. He first offered the hypothesis of the possibility of the disintegration of tritium: ${}_1H^3 \longrightarrow {}_2He^3 + e^-$ with the formation of a helium isotope. At the same time, Bleakney and his colleagues (23-25), having received negative results from the study of an exact mass spectograph, also came to the conclusion that the hydrogen isotope with a mass of 3 is not found in any noticeable quantities in nature (the ratio of H^3 to H^1 is of the order 10^{-12}).

In 1939, Alvarez and Cornog (24), studying the nuclear reaction which takes place upon the bombardment of deuterium with deuterons, discovered the radioactivity of the produced gas, which they identified as hydrogen. In subsequent publications (25), these authors confirmed their hypothesis that the hydrogen isotope that is produced by the nuclear reaction ${}_1D^2 + {}_1D^2 \longrightarrow {}_1H^3 + {}_1H^1$ is radioactive. They subjected heavy water to electrolysis after it had been irradiated by deuterons and discovered radioactivity in the gas produced on the cathode, while the oxygen produced on the anode had no activity. The half life was measured in three tests, one of which lasted for 80 days; it was roughly estimated at 150 ± 40 days; however, later, more exact measurements of other authors (26) have established the half life of tritium at 31 ± 8 years.

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II. DETERMINATION OF THE ENERGY OF BETA RADIATION OF TRITIUM

On the basis of measurements of the ratio of the number of active atoms to the number of ion pairs formed in a given volume of gas, Alvarez and Cornog (25) established that the approximate average energy of beta particles radiated in the disintegration of tritium ${}_1H^3 \longrightarrow {}_2He^3 + e^-$ is 10 KeV. At the same time Libby and Lee studied the beta radiation of a piece of beryllium that had been bombarded by deuterons in a cyclotron for several months. The maximum radiation energy was found to be 13 ± 5 KeV. The authors attributed the beta radiation to the isotope of Be^{10}, and not to the tritium formed here. Shortly afterward, O'Neal and Goldhaber (27) confirmed the fact that, after bombardment of a beryllium target with deuterons with an energy of 1 MeV, radiation is observed with a maximum energy close to 13 ± 5 KeV. However, they showed that it is impossible to discover this beta radiation in beryllium precipitate obtained after chemical processing of the target to identify the radioactive isotope of beryllium. It appeared that the radioactivity belonged to the gas extracted from the beryllium target by heating or dissolving in sulphuric acid. O'Neal and Goldhaber came to the conclusion that the observed activity was due to the hydrogen isotope, tritium, formed according to the equation $Be^9 + D^2 \longrightarrow Be^8 + H^3$.

Later, these authors (28) were concerned with the study of the disintegration constant of tritium. Unfortunately, it cannot be determined by the ordinary method from a disintegration curve because of its small magnitude. The authors used another method based on the possibility of determining the disintegration constant λ from the ratio $\lambda = N'/N$, where N is the number of H^3 nuclei formed, and N' is the number of H^3 nuclei which disintegrate in a unit of time. Tritium was obtained by irradiating lithium with slow neutrons which led to the reaction $Li^6 + n^1 \rightarrow He^4 + H^3$. Metallic lithium, scattered in a thin glass tube, was set in a large piece of paraffin and placed in a certain position toward the source of neutrons (radon beryllium tube), where it was kept for 4 months. (In other tests the authors used a three-week bombardment of a lithium target with slow neutrons in a Michigan cyclotron. The activity of the hydrogen obtained in this way was 100 times greater than that obtained by the previous method.) The lithium was then treated with water and the liberated hydrogen collected; thus, tritium was extracted with a yield of 94 percent. A specific small quantity of this hydrogen with an admixture of alcohol vapors was placed in a Geiger counter where its activity was determined, according to which the Number N' was calculated. The total number N of formed tritium nuclei was determined by special tests with the calculation of the number of neutrons absorbed by a piece of lithium.

In this way it was determined that λ is equal to 7.10^{-10} seconds $^{-1} \pm$ 25 percent, which gave 31 ± 8 years as the half life of tritium. The energy of beta radiation was determined by those authors at 15 ± 5 KeV.

Brown established the length of flight of beta particles of tritium in helium at 13 ± 1 mm by using a specially constructed Geiger counter filled with helium at atmospheric pressure, thus permitting the detection of radiation with low energy. Comparing the relationship between the length of flight of directed rays and their energies, the author evaluated (by analogy) the energy of beta particles which are radiated by tritium to be 9.5 ± 2 KeV. Nielsen (30) obtained data close to this by using a Wilson cloud chamber; he estimated the maximum energy of beta particles

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at 14.5 ± 1 KeV. Finally, a short time ago Watts and Williams (31) used a different method for determining the maximum energy of beta particles: A Geiger counter with a small thin window of several colloidial films was used; rays of electrons radiated by a heated tungsten wire flowed through this window; the electrons were first accelerated by superimposing a certain potential. It appeared that upon superimposing an accelerating potential of 12 KV, the electrons of the wire penetrated the window ("thickness" of the window). Then a source of beta rays was placed before the window in a vacuum on an appropriate electrode, on which an accelerating or delaying potential had been superimposed. By varying this potential, the magnitude at which the beta rays began to penetrate the window was found. From the obtained magnitudes of the "thickness" of the window and the potential necessary for stopping beta rays, the maximal energy of the beta particles was calculated.

The source of beta rays of tritium was prepared by the following method: an aluminum disc (electrode) was tempered at 500 degrees in an oxygen atmosphere, cooled in a vacuum and then treated by water vapor containing tritium water (T_2O). The water reacted with a thin film of aluminum oxide on the electrode; hydration took place with the formation of $Al(OT)_3$; the water fixed in this way is not removed even in evacuation. The disc served as an electrode on which a certain potential was superimposed. It appeared that with high accelerating potentials the intensity of beta radiation in the counter was very great and fell almost to zero with a lowering of the superimposed potential to 1 KV. Thus, the upper limit for the energy of beta particles of tritium was determined in these experiments as 12—1 = 11 ± 2 KeV, which is close to the determination of other authors. The shortcoming of this work is that the measurements were made on only one window without varying its thickness.

A comparison of different authors' measurements of the maximum energy of beta particles of tritium is presented in Table 1.

Table 1. Energy of Beta Radiation of Tritium

Investigator	Method of Determination	Energy (KeV)
Libby and Lee (26)	Magnetic	13 ± 5
Alvarez and Cornog (25)	Ion pairs	10
O'Neal and Goldhaber (28)	Length of flight in a mixture of alcohol and argon	15 ± 3
Brown (29)	Length of flight in helium	9.5 ± 2
Nielsen (30)	Droplets in a Wilson camera	14.5 ± 1
Watts and Williams (31)	Passage of beta rays through a certain thickness of the window of a counter	11 ± 2

III. METHODS OF OBTAINING TRITIUM

The following methods of obtaining tritium are the most common:

1. Bombardment of deuterium with deuterons (17) in a cyclotron leads to the nuclear process: $D^2 + D^2 \rightarrow H^3 + H^1$; $Q = \pm 3.97 \pm 0.02$ MeV;

2. Bombardment of beryllium with deuterons (26, 27) also leads to

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tritium: $Be^9 + D^2 \rightarrow Be^8 + H^3$;

3. Irradiation of lithium with slow neutrons, expressed by the equation: $Li^6 + n^2 \rightarrow He^4 + H^3$.

In addition, there are other nuclear reactions which lead to the production of tritium:

4. Cornog and Libby (32) bombarded saturated water solutions of boric acid and ammonium nitrate (containing an excess of salts in crystal form) with slow neutrons with an energy of 20 MeV. The water vapors of these solutions showed an activity of approximately 10^4 impulses/second per mole in a Geiger counter, while vapors of distilled water produced less than 5 percent of this activity under these conditions. The authors think that the following nuclear reactions take place:

$${}_5B^{10} + {}_0n^1 \rightarrow [{}_5B^{11}]^* \rightarrow {}_4Be^8 + {}_1H^3; \quad Q = +0.2 \text{ MeV};$$

$${}_5B^{11} + {}_0n^1 \rightarrow [{}_5B^{12}]^* \rightarrow {}_4Be^9 + {}_1H^3; \quad Q = -9.6 \text{ MeV};$$

$${}_7N^{14} + {}_0n^1 \rightarrow [{}_7N^{15}]^* \rightarrow {}_6C^{12} + {}_1H^3; \quad Q = -4.3 \text{ MeV};$$

$${}_7N^{14} + {}_0n^1 \rightarrow [{}_7N^{15}]^* \rightarrow 3\,{}_2He^4 + {}_1H^3; \quad Q = -11.5 \text{ MeV}.$$

Using Segre and Jockey's unpublished data on the output of one neutron for 200 deuterons (in the bombardment of a beryllium target with deuterons with an energy of 16.5 MeV producing the nuclear reaction: $Be^9 + D^2 \rightarrow Be^{10} + {}_0n^1$) in a 60-inch cyclotron and considering the half life of tritium as 31 years (28), the authors estimated the effective size of a slow neutron in the above tritium producing reactions as approximately 10^{-26} sq cm (with a possible five-point error).

5. L. Borst (33) described the nuclear reactions which take place in the irradiation of nitrogen and flourine with deuterons with an energy of 8.2 MeV. These reactions are accompanied by the formation of tritium:

$$N^{14} + D^2 \rightarrow N^{13} + H^3; \quad Q = -4.5 \pm 0.2 \text{ MeV};$$

$$F^{19} + D^2 \rightarrow F^{18} + H^3; \quad Q = -4.1 \pm 1.1 \text{ MeV}.$$

It has been established that neutrons (34) are formed in relatively great quantities in the atmosphere as a result of cosmic radiation: $N = 0.8$ neutrons (per second) per 1 sq cm of the earth's surface. Not long ago Libby (35) offered the hypothesis that the H^3 helium isotopes in the atmosphere owe their origin to the tritium formed according to the above-mentioned nuclear reactions of neutrons with atmospheric nitrogen:

$$N^{14} + n^1 \rightarrow C^{12} + H^3.$$
$$N^{14} + n^1 \rightarrow 3\,He^4 + H^3.$$

The disintegration of tritium leads to the formation of a helium isotope

$$H^3 \rightarrow He^3 + e^-.$$

The half life of tritium of 31 years is very short from the geological point of view. Considering the age of the earth as $1.5 \cdot 10^9$ years, the

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author calculates the helium isotope content of the atmosphere as $1.3 \cdot 10^{-11}$ cc He^3 per 1 cc of air.

IV. PROPERTIES OF TRITIUM

A. Elasticity of Vapor of Liquid Tritium

Libby and Barter (36) determined the elasticity of vapor of liquid isotopes of hydrogen HT and DT by fractionation and determination of the radioactivity of various portions of the distilled gas. One to five liters of hydrogen containing 10^{-9} moles of HT or DT per mole of H^2 or D^2 was used for fractionation. Radioactive hydrogen was obtained by irradiating lithium with neutrons in a Berkeley cyclotron for several months and then processing the lithium target with water on D^2O. HT or DT is precipitated in this treatment.

The activity was measured with a Geiger counter which was filled with hydrogen or deuterium at a pressure of 15 mm Hg with an admixture of ethyl alcohol vapors (2-3 mm Hg pressure). A uranium standard was used to check the measuring apparatus.

The results are compared with literary data for D^2 and H^2 in Table 2 (data for T_2 is extrapolated on the curve in Figure 1).

Table 2. Elasticity of Hydrogen Isotope Vapors

Molecule	Elasticity of Vapor at 20.4 degrees K (mm Hg)	Reference in Literature
H_2	760	—
HD	438	37
D_2	256	38
HT	254 16	
DT	123 6	36
T_2	45 10	

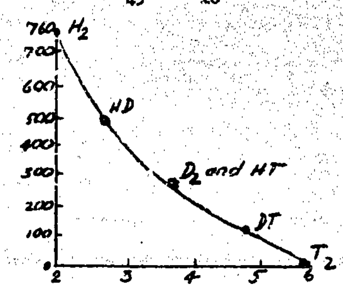

Figure 1. Elasticity of hydrogen isotope vapors is measured along the ordinate axis (in mm Hg) at 20.4 degrees K. The mass of the molecule is measured along the abscissa.

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The data shows that tritium can be easily separated out by distillation of liquid hydrogen isotopes if the obtained mixture is previously run through an appropriate catalyzer to establish the equilibrium:

$$2\,HT \rightleftharpoons H_2 + T_2;$$

$$2\,DT \rightleftharpoons D_2 + T_2.$$

Since the Van der Waals' force of cohesion in liquid hydrogen must be the same for all isotopes, the observed dependence of the elasticity of vapor upon the mass of the isotope is apparently due to the difference in the neutral energies which are expressed in the following magnitudes (39):

Isotopes:	H_2	HD	D_2	HT	DT	T_2
Free energy (in large calories per mole):	6.253	5.423	4.433	5.114	4.049	3.625

B. Magnetic Moment

Sacks and Schwinger (40) have determined the magnetic moment, which was 2.68 tritium and -1.84 for He^3.

C. Equilibrium of a Tritium Water System

Libby (39) calculated the equilibrium constants of such a system theoretically from the fact that forces acting inside a molecule do not change with a change in the mass of the nucleus and that any effect in the properties of the molecule is due to the different masses which are moving in the same field of force. Study of the equilibrium of such a system is of interest from the point of view of isotope exchange.

Black and Taylor (41) studied this system experimentally, using Pt as a catalyzer on carbon. Radioactive water was placed with a catalyzer in a reaction vessel which had a water jacket to maintain a certain temperature. Hydrogen circulated through this water in a closed system until it reached equilibrium. The water vapors were then frozen and separated from the gas and one-half ounce placed in a Geiger-Mueller counter. The mixture for the readings was always composed of water vapors (partial pressure 2 mm Hg), 2.4 mm Hg alcohol vapors, 8-20 mm Hg hydrogen, and 20 mm Hg argon. The counter was given a preliminary check with a standard uranium specimen. No further change of the concentration took place after equilibrium had been reached on the catalyzer in accordance with the fact established by Gould, Blealoney, and Taylor (43) that an exhange between hydrogen isotopes and water is not catalyzed by glass. Equilibrium constants were calculated according to the equation

$$k = \frac{[HTO] \times [HH]}{[HT] \times [HHO]} = \frac{[HTO] / [HHO]}{[HT] / [H\,H]}$$

The partial pressures of the components were determined by a counter: the partial pressure of HTO (or HT) in a given vessel is proportional to the number of disintegrations of these substances in a unit of time. Considering that the actual concentration of tritium in a portion of water or hydrogen was 10^{-21} moles, the total pressure of a portion of

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radioactive hydrogen or water vapors can be considered as a partial pressure of the inactive components. Therefore, having separated the hydrogen (active and inactive) -- after equilibrium had been established -- from the water vapors (active and inactive) and then placing them one after the other in the same counter, where the pressure, volume, and number of impulses per minute were measured, the necessary data for the calculation of the equilibrium constants was obtained. The ratio of the number of impulses per minute to the pressure of water vapors in millimeters of Hg gives the ratio HTO / HHO, and the ratio of the number of impulses per minute to the partial pressure of hydrogen gives HT / HH.

The data obtained in such a manner for a number of temperatures is presented in Table 3, where it is compared with Libby's (39) theoretical data obtained from the calculation of vibration frequencies.

Table 3. Equilibrium Constants of a System

	Equilibrium Constants		
Temperature (in degrees C)	Experimental Value	Calculation According to the Formula in Table 4	Libby's Theoretical Values
16	6.75 0.04	6.73	6.47
20.2	6.47 0.12	6.50	6.24
25	6.25 0.05	6.25	6.01
56.2	5.05 0.05	5.02	4.84
79.6	4.37 0.05	4.40	4.23
111.2	3.76 0.04	3.77	3.64
158.4	3.10 0.06	3.12	3.03
217.1	2.64 0.04	2.61	2.54
302.9	2.17 0.02	2.17	2.08

Comparison of the experimental data with the theoretical calculations shows a sufficiently close agreement. As a result of these experiments, the authors could obtain all the thermodynamic data for this system (Table 4).

1) $\log K = 0.292 \log T + \frac{336.5}{T} - 1.055$

2) $\Delta S^0 = 1.34 \log T - 4.25$

3) $\Delta F^0 = - 4.38\ T - 1.34\ T \log T - 1540$

4) $\Delta C_p = 0.58 \pm 0.05$ small calories/mole

5) $\Delta H^0 = 0.58\ T - 1540$

6) $\Delta H^0_0 = - 1540 \pm 160$ small calories/mole

V. ANALYTICAL METHOD OF DETECTING TRITIUM

The detection of tritium is very difficult because of the extremely weak energy of the beta radiation, which is only about 0.015 MeV. This makes it necessary to use specific methods for measuring the radioactivity of tritium. Usually it is measured in a gaseous or vapor form, which is placed in a Geiger counter or ionization chamber as a charging gas. For

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example, Ruben and his colleagues (42) placed a mixture of tritium with hydrogen in a Geiger counter; the accuracy was not greater than 10-15 percent under these conditions because hydrogen is not a satisfactory "counter" gas. Frequently gaseous "counter" mixtures with vapors of alcohol (36), argon (42, 43), butane (45), etc., are used for measuring.

A short time ago Henriques and Margnetti (46) described a specially developed method for detecting tritium in organic compounds with an accuracy of 2 percent. They used a quartz ionization chamber connected with a Lauritsen electroscope. The authors used this device successfully to detect a radioactive isotope of C^{14} in the form of carbonic acid (47). Tritium was obtained in a cyclotron by irradiating a water-cooled beryllium target with deuterons. Two nuclear reactions took place, leading to the formation of tritium:

$$Be^9 + H^2 \longrightarrow H^3 + 2\,He^4;$$

$$H^2 + H^2 \longrightarrow H^3 + H^1$$

The beryllium target was then placed in a quartz tube connected to a vacuum system and heated for 15 minutes in a hydrogen atmosphere. The liberated mixture of tritium and hydrogen was passed over cupric oxide which was heated to 300 degrees and the radioactive water which was formed was condensed in a trap; thus 99 percent of the tritium found in the target was changed to T_2O.

The general method of analysis consists in burning the tested substance over cupric oxide with the formation of water, which is then dissolved with a magnesium amalgam at 400 degrees for one hour to separate the hydrogen isotopes.

An ionization chamber is charged with 10 millimoles of radioactive hydrogen mixture at atmospheric pressure. According to the authors, this method can quantitatively detect approximately 10^{-4} microcuries (10^{-14} moles) of tritium in 10 millimoles of hydrogen, which greatly surpasses the analytical possibilities in work with deuterium. (A curie is a unit of radioactivity equivalent to the activity of one gram of radium or any substance with an equivalent radioactivity. This quantity gives $3.6\cdot10^{16}$ disintegrating atoms per second. A microcurie corresponds to that quantity of a radioactive substance which disintegrates $3.6\cdot10^4$ atoms per second, which corresponds to $2.16\cdot10^6$ impulses/minute. Considering the half life of tritium of 30 years as $1.6\cdot10^7$ minutes, then $36\cdot10^{-8}$ of any amount of the substance disintegrates in one minute; with one mole of tritium we would have $1.8.10^{16}$ impulses/minute. Thus, a microcurie of tritium corresponds to 10^{-10} moles of tritium.) This method was checked with radioactive benzene, which was prepared by the reaction of the exchange of benzene with TH on a nickel catalyzer according to the Polanyi (48) method.

Tests were made with various concentrations of radioactive benzene in ordinary benzene, where the least activity of usable specimens (approximately $3\cdot10^{-4}$ microcuries of tritium) was used as a unit. The relative accuracy of measurements is shown in Table 5, where the radioactivity R_T is expressed as a ratio of the activity to the control (background), and R_1 is the radioactivity calculated from the ratio of concentration of the radioactive benzene specimen.

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Table 5. Results of Measuring the Activity of Tritium in an Ionization Chamber

Relative Concentration of Tritium	Radioactivity Observed R_H		Calculated R_1	Average Deviation (in %)
259	474) 479)	avg 476	472	0.7
65.7	117.4) 120.7)	avg 119	120	0.8
14.6	26.6) 25.8)	avg 26.2	26.5	1.1
83.79	7.06) 6.87)	avg 6.97	6.90	0.9

The authors did not observe the dissipation of a radioactive isotope in the process of analysis.

Other methods used in detecting tritium are referred to in the accounts of other work using tritium as a radioactive indicator. (For a description of various types of counters see item 49 in the bibliography.)

VI. USE OF TRITIUM AS AN INDICATOR IN CHEMICAL REACTIONS

The research of Ruben and his colleagues explaining the mechanism of a number of complex reactions was the first work in this field.

A. Oxidation of Fumaric Acid

The oxidation of fumaric acid by permanganate in a sulphuric acid medium at 35-50 degrees leads to the formation of formic acid and carbonic acid according to the equation

$$COOH - CH{=}CH - COOH + 2MnO_4 - 6H - 3CO_2 + HCOOH + 2Mn^{++} + 4H_2O.$$

The speed of oxidation of formic acid is considerably less under these conditions. The mechanism of this process is not clear; in particular, it is not known whether the formic acid is formed from the methenyl or carboxylic carbon and whether or not the hydrogen is transferred from the methenyl carbon. Allen and Ruben (50) solved this problem by using radioactive indicators: C^{11} (with a half life of 20.5 min) and tritium. For this purpose the authors developed a method of rapid synthesis of radioactive fumaric acid containing C^{11} in the carboxyl through the stages of transformation: $C^{11}O_2$ — $KC^{11}N$ — nitrile of succinic acid -- succinic acid and, finally, dehydrogenation of the latter with dehydrogenase into fumaric acid. This synthesis took 2 hours, and thus sufficient radioactivity of the preparation was preserved to study its process of oxidation. Oxidation by permanganate was made in a current of nitrogen with the carbonic acid being carried off and absorbed by the calcium hydroxide. The radioactivity of the precipitated calcium carbonate was then measured and found to be very high. After

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precipitation the formic acid formed in oxidation was oxidized by alkaline permanganate (in comparison with an acid solution, the reaction is very rapid in an alkaline solution) to carbonic acid, which is absorbed by $Ca(OH)_2$; the radioactivity of the precipitated calcium carbonates was checked. This carbonate was absolutely inactive, indicating that formic acid is formed from the methenyl carbon in oxidation of fumaric acid.

To explain the second question -- the genesis of hydrogen in the formic acid formed -- the authors studied the exchange of hydrogen between formic acid and radioactive sulphuric acid in the process of its oxidation by permanganate. They used 1.5 N-tritium-sulphuric acid with an activity of $9 \cdot 10^7$ impulses-minute per gram atom of hydrogen. After the reaction of the oxidation a sulphate ion was precipitated out using $BaCl_2$, and the water and formic acid were removed in a vacuum and separated into two portions: in one the activity of the formic acid was determined by the method described above (burning to CO_2; precipitation using $Ca(OH)_2$ and separation of the water from $CaCO_3$), and in the second by neutralizing the soda, separating the water in a vacuum and burning the hard sodium formate. The activity of the hydrogen separated from this water was also checked. The authors measured the radioactivity of tritium by placing a mixture of argon with 10 percent ethyl alcohol vapors and water vapors (3 mm Hg) or a mixture of hydrogen with ethyl alcohol (15 mm Hg) in a Geiger-Mueller counter. The water formed in both cases was weakly active; it had only 2 ± 1 percent of the activity of the sulphuric acid used.

These results indicate that the bond between carbon and hydrogen in the methine group is not broken in the formation of formic acid during oxidation of the formic acid in spite of the profound transformation of its molecules.

B. Study of the Menshutkin Reaction

Harman, Stewart, and Ruben (42) have attempted to explain the mechanism of the course of the famous Menshutkin reaction

$$R_3N + RX \longrightarrow [R_4N]^+ + X^-,$$

which has repeatedly attracted the attention of many investigators because of its unusual kinetics. The equation of speed of this reaction contains a probability factor P ("steric factor") with a very small magnitude, which varies considerably depending upon the solvent, though it usually is close to unity.

$$\frac{d[X^-]}{dt} = K[R_3N][RX] = Pze^{-E/RT}[R_3N][RX].$$

For example, for the reaction between aniline and $C_6H_5COCH_2Br$, this factor changes from $4 \cdot 10^{-11}$ in benzene to $5 \cdot 10^{-5}$ in benzyl alcohol. Gol'dshmidt and Vorob'yev (51) have studied the kinetics of the reaction between dimethyl aniline and bromotoluene in various solvents; Table 6 gives an idea of the change of the kinetics depending upon the solvent.

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Table 6. Kinetic Data for the Reaction of Dimethyl Aniline With Bromotoluene in Different Solvents

	Solvent			
	Acetone	Phenyl-acetone	Nitro-Benzene	Ethyl Alcohol
$k \cdot 10^4$ (at 30° C)	80.5	84.5	118	650
E	9747	9929	11200	13800
− log P	4.94	5.08	6.16	8.78

The small magnitude of P in the Menshutkin reaction apparently indicates a low coefficient of effectiveness of the collisions leading to the reaction. In order to explain this phenomenon Moelwyn-Hughes and Sherman (52) have suggested that at least one of the reagents forms an unstable complex with the solvent and that this complex is the actual reagent; thus an evaluation of the product $[R_3N]\,[RX]$ in the equation of speed may have an error, which is reflected in the magnitude of P. (Gladyshev and Syrkin (53) showed in the example of the interaction of triethyl amine with CH_3J that the steric factor maintains its low value also in the reaction in the gaseous phase in the absence of a solvent. The authors examined this question from the point of view of the theory of the transition state.) The idea of the formation of an intermediate complex in the reaction, which under favorable conditions then produces a stable product of the reaction was expressed by a number of authors (54). For solutions in benzene, where the reaction products are poorly soluble, Edwards (55) suggested that the reaction first proceeds rapidly and is reversible, but the speed of the general reaction is determined by the formation of the precipitates:

$$R_3N + RX \rightleftarrows (R_4N)^+ + X^- \longrightarrow R_4NX \text{ hard.}$$

In the solution the equilibrium is shifted toward the initial components.

Ruben and his colleagues proceeded from the following premises in their research: If the nature of an intermediate product of a reversible reaction is such that all alkyl groups in it are equivalent with regard to an ion of a haloid (for example, $(R_4N)^-$) until they pass through the reverse reaction, then in making a reaction with an alkyl group containing a radioactive indicator (for example C^{11} or H^3), we must obtain radioactivity in the non-reacted amine and in the final product (the asterisk with R indicates the radical which contains the radioactive atoms):

$$R_3N + R^*X \rightleftarrows \left[\begin{array}{c} R \\ | \\ R - N - R^* \\ | \\ R \end{array} \right]^+ + X^- \rightleftarrows R_2R^*N + RX.$$

To check this condition, the authors synthesized a radioactive methyl iodide containing tritium according to the following methods:

(a) $HCOOH + CH_3OH \longrightarrow HCOOCH_3 + H_2O$;

(b) $HCOOCH_3 + HT \longrightarrow CH_3OH + (CH_2T)\,OH$ (temperature 160 degress, copper-chromium catalyzer);

(c) $(CH_2T)\ OH + HJ \longrightarrow HC_2TJ + H_2O$.

Approximately 2 gr TCH_2J were obtained with a 75 percent product. Another specimen of radioactive methyl iodide containing C^1 (half life

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20.4 minutes) was also synthesized by the authors. They then studied the reaction between the produced tritium-methyl iodide and dimethyl aniline and trimethyl amine in alcohol and benzene solutions. An excess quantity of amine of three and five times was used for this, which after a 3-hour reaction was separated from the remaining components and tested for tritium content. An absolutely insignificant amount of tritium was found in the amine, with less than 1 percent activity, which was expected on the basis of proportional distribution. All the radioactivity in the product was formed from the reaction (salts). These results were obtained for both amines used in the two solvents.

The authors conducted tests of the exchange between radioactive salt and trimethyl amine for 8 hours in alcohol and 3 days in benzene, assuming the possibility of the exchange process:

$$R_3R^* NX + R_3N \rightleftharpoons R_4 NX + R_2R^*N.$$

However, no exchange was discovered. The authors concluded from this that intermediate products (b) of the Menshutkin reaction which are formed quickly and reversibly and in which the haloid ion loses its bond with the methyl radical are not formed in the cases studied.

C. Exchange of Tritium in Amines

Fontana (44) also studied the exchange reactions with tritium and deuterium using complex aromatic amines. Ingold and his colleagues (55) were the first to show that such amines and phenols are capable of exchanging hydrogen (in ortho- or parahydrogen) in catalysis by alkalis in the case of phenols or acids in the case of amines. It was supposed that the presence of quinoidine resonance forms of free amines or phenol creates the condition for the mobility of the hydrogen atom. The authors used tritium and deuterium to study the mobility of the hydrogen atom in such molecules. Water containing tritium was obtained with a 60-inch cyclotron. The water had an activity of 600 microcuries per mole. In carrying out the exchange reaction it was diluted by ordinary water 1,000 times. The radioactivity was determined by passing a mixture of 10 mm Hg of water vapors and 20 mm Hg propane through a Geiger counter. As a result of the research it was shown that the exchange reaction of tritium (and deuterium also) takes place very slowly at room temperature. For example, crystal violet containing tritium loses only approximately 2 percent of its original activity in a 2 percent water solution during 3 months. At 100 percent [Sic. Probably should be 100 degrees], however, 60 percent of the original activity is lost over a 7-day period with the addition of sulphuric acid as a catalyzer. Thus it was shown that the mobility of hydrogen appears principally at high temperatures and in the presence of catalyzers.

D. Role of Chlorophyl in Photosynthesis

Very little is known about the role of chlorophyl in the photosynthesis process of green plants. The theories evolved by various authors in this field can be reduced basically to two main concepts: (a) chlorophyl takes the role of a restoration agent (donor of hydrogen) and (b) the action of chlorophyl is analogous to the action of sensitizers in photosensitive emulsions. The first concept has more adherents; for example, Stoll (56), Willstaetter (57), and others attribute to chlorophyl (GH_2) the function of a donor of hydrogen in photochemical reactions, where monohydrochlorophyl GH is formed. This is a free radical which then

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is transformed in another photochemical reaction to chlorophyl: $GH + H_2O + h\nu \longrightarrow GH_2 + OH$. A number of other authors (58, 59) also suggest analagous reactions of oxidation and restoration. It was possible to determine whether or not chlorophyl was a donor of hydrogen by using tritium as an indicator. Norris, Ruben, and Allen (60) reasoned from the following premise: If photosynthesis is allowed to take place for a sufficiently long time in radioactive water containing tritium, then radioactive chlorophyl must be formed if chlorophyl actually plays the part of a donor of hydrogen in photosynthesis.

In the first series of experiments the authors used Chlorella pyrenoidosa, which was irradiated for 3 hours in a bicarbonate water solution containing HTO. The radioactivity of this solution was $1.7 \cdot 10^8$ impulses/min per mole of H_2O, and each cubic centimeter of Chlorella contained $2 \cdot 10^{-5}$ moles of chlorophyl. The results of these experiments are given in Table 7.

Table 7

Duration of Exposure (in min)	Quantity of Chlorophyl (in moles)	Quantity of Precipitated O_2 (in moles)	Radioactivity (impulses/min) Observed	Calculated*
175	$2 \cdot 10^{-4}$	$2.0 \cdot 10^{-3}$	80	2,200
185	$6 \cdot 10^{-5}$	$0.5 \cdot 10^{-3}$	65	5,260
180	$11 \cdot 10^{-4}$	--	100	9,350

* Calculated on the hypothesis that each molecule of chlorophyl has one mobile hydrogen atom which is capable of exchange with tritium.

These results do not provide a basis for concluding that photochemical exchange takes place between chlorophyl and the hydrogen ion (tritium) of water.

The second series of experiments was conducted with pure chlorophyl. Radioactive water was added to a portion of very pure chlorophyl (97 percent) which had been dissolved in alcohol. After having been stirred for 30 minutes in the light, the solvents were removed in a vacuum over the course of several days and the chlorophyl was burned. The water which was formed was broken down with the separation of hydrogen, which was placed in a counter to determine its activity. The results of this series of experiments are presented in Table 8.

Table 8

Quantity of Chlorophyl (in mg)	Specific Activity of H_2 (impulses/min per gr atom of H)	Duration of Exposure (in min)	Radioactivity (impulses/min) Observed	Calculated
40	$2.72 \cdot 10^8$	30	187 ± 30	3,820
95	$0.53 \cdot 10^8$	60	51 ± 20	2,430
34	$2.78 \cdot 10^8$	30	100 ± 25	3,240

Thus, less than 5 percent of the expected exchange took place in these experiments also. In evaluating this data it must be considered that the kinetics of the reaction may differ with different hydrogen isotopes because of the difference in zero energies of bond and thus

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in the energies of activation. Unfortunately, the duration of these experiments was very short. An example of such an isotope effect is presented by the results of the study by Rollefson and A. and L. Farkas (13) of the speed of the reaction:

$$Cl + H_2 \longrightarrow HCl + H$$
$$Cl + D_2 \longrightarrow DCl + D$$

the energies of activation of which differ by 1,630 small calories.

Although the results of the study by Norris, Ruben, and Allen are of great interest, they cannot be accepted as decisive in evaluating the correctness of the theory of the rule of chlorophyl as a donor of hydrogen in photochemical reactions in plants.

E. Mechanism of Alkylation in the Liquid Phase

The processes of alkylation are connected with the transfer of hydrogen, for example:

$$(CH_3)_3\ C - H + H_2C = C\,H_2 \longrightarrow (CH_3)_3\,C - CH_2 - CH_3$$

(See Ciapetta (62) and Egloff (63)).

It is important to explain the role which the catalyzer plays in these reactions and whether or not it is a carrier of hydrogen.

Stewart and Harman in their recent work (64) attempted to explain the presence of the transfer of hydrogen in the alkylation of isobutane by 2-butene using sulphuric acid as a catalyzer. It was important to determine previously the degree of hydrogen exchange which takes place between the different components of the reaction and the catalyzer (sulphuric acid containing tritium). The radioactive sulphuric acid had a specific activity of $5.43 \cdot 10^7$ impulses/min per mole.

Forty cubic centimeters and 6 cc of 100 percent tritium sulphuric acid were stirred briskly for 20 minutes at 10 degrees in a load reactor. The isobutane was then seperated and burned over cupric oxide. The water which formed was broken down over magnesium at 600 degrees and the hydrogen separated out in this process was placed in a Geiger counter to determine its activity (see item 42 in the bibliography). The specific activity of the hydrogen obtained in such a manner was $1.36 \cdot 10^5$, which was only approximately 7 percent of the calculated value, deviating from a uniform distribution of tritium between sulphuric acid and the hydrogen of isobutane attached to the third carbon. An analogous test was made of the exchange between tritium sulphuric acid and 2-butene. To prevent the absorption of the 2-butene by the sulphuric acid the gas was diffused through the 6 cc of H_2SO_4 with such a speed that absorption took place only to a slight degree. All the butylene which was passed through the sulphuric acid was collected in a trap in liquid air, it was processed further, as described above, to determine its activity, which was $6.1 \cdot 10^5$, i.e., significantly greater than for isobutane, despite the fact that the period of contact of the butylene with sulphuric acid was very short (it is not shown by the authors), while for isobutane it was 20 minutes.

These experiments show that the exchange of hydrogen in butylene takes place very rapidly and that there is equilibrium absorption of

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hydrogen in sulphuric acid. It is possible, however, that the exchange originates in the process of polymerization of butylene in sulphuric acid according to equilibrium $2C_4H_8 \rightleftharpoons C_8H_{16}$.

The following series of experiments consisted of carrying out the alkylation process with a separation of the liquid products of the reaction and determination of their activity.

A mixture of 0.48 moles of isobutane and 0.109 moles of 2-butene was added to 0.131 moles of 100 percent tritium sulphuric acid (specific activity $5.43 \cdot 10^7$) over a 15-minute period while it was mixed under pressure in an iron vessel lined with lead at 10 degrees. After several minutes the excess isobutane was removed. The hydrocarbon layer was separated after stratification, washed with water, dried, and then fractionated on a column (20 theoretical plates; volume of liquid, 20 cc). Two fractions and residues were selected. The activity of each fraction and residue was determined by the method described above.

It was made clear that the activity of different fractions was practically the same. As the above-described tests of exchange have shown, it is possible to calculate what the activity would be with a uniform distribution of tritium among all the hydrogen atoms in 2-butene prior to the process of alkylation, taking into consideration the high speed of hydrogen exchange. If all atoms of tritium are uniformly distributed between the sulphuric acid and the butene, then the activity of the hydrogen from the butylene obtained is expressed as follows: $5.43 \cdot 10^7 \cdot \frac{2 \cdot 0.131}{(8 \cdot 0.109) + (2 \cdot 0.131)} = 1.25 \cdot 10^7$ impulses/minute per mole (taking two atoms of hydrogen in H_2SO_4 and eight atoms of hydrogen in butylene). As a result of alkylation, the activity of the hydrogen from the alkylate must decrease further. Considering that the molecules of active butylene are combined in alkylation with molecules of isobutane in a ratio of 1:1, the specific activity of hydrogen obtained from such alkylate is $1.25 \cdot 10^7 \cdot \frac{8}{18} = 5.5 \cdot 10^6$. This magnitude is close to that obtained experimentally for a fraction of alkylate. The agreement of the calculated and experimental magnitude is even closer with regard to the "residue," i.e., to the high boiling products which compose the basic mass of the alkylate. It is supposed that polymerization of butylene precedes the alkylation, and then the product of dimerization is combined with the isobutane as follows:

$$2\,C_4H_8 \rightarrow C_8H_{16};\; C_8H_{16} + C_4H_{10} \rightarrow C_{12}H_{26}.$$

Then the activity of the obtained alkylate must be: $1.25 \cdot 10^7 \cdot \frac{16}{26} = 7.7 \cdot 10^6$, which almost agrees with the observed magnitude of $7.6 \cdot 10^6$. The authors conclude from this that intermediate products of the polymerization of butylene have a longer period of stability than the octanes which are formed and this together with the greater speed of polymerization contributes to the formation of heavier products and causes a more even distribution of tritium.

F. Isomerization of n-Butane and Isobutane

Powell and Reid (15) made a detailed study of the mechanism of an analogous type of reaction. They studied the stages of the process of isomerization of n-butane in isobutane using aluminum chloride as a catalyzer $CH_3-CH_2-CH_2-CH_3 \rightleftharpoons CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$

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This process is also connected with the transfer of hydrogen, and as a number of investigators (65-67) have shown, the presence of hydrogen halide of moisture insuring the formation of HCL (HBr) plays a very important role in catalysis by aluminum chloride (bromide). Absolutely dry haloid salts do not catalyze in the absence of HCl. To explain the mechanism of the transfer of hydrogen in this reaction, the authors used tritium, introducing it both into the molecules of butanes and into hydrogen chloride.

Tritium was obtained in the form of water by bombarding heavy water with deuterons in a 60-inch Berkeley cyclotron. The water obtained had a specific activity of $5 \cdot 10^9$ impulses/minute per mole. After acidification the water was subjected to electrolysis on Pt-electrodes to obtain tritium. Radioactive hydrogen chloride was prepared either by direct combination of tritium with chlorine at 300 degrees on activated charcoal or by the interaction of radioactive sulphuric acid with sodium chloride. Radioactive butanes containing tritium in a definite place of the molecule were prepared by hydrolysis of the appropriate butylmagnesium bromide by an acid solution of radioactive water; the gases which were formed were then carefully rectified.

The catalyzer was prepared by saturation of aluminum oxide or activated charcoal with aluminum chloride in a hydrogen chloride atmosphere at 316 degrees.

The radioactivity was measured by a Geiger-Mueller counter. Butane proved to be a satisfactory gas for the counter, but the admixture of hydrogen was usable only in small quantities. Therefore, the analysis of tritium in the tests of the exchange of hydrogen with radioactive butane was conducted in the following manner: Butylene (obtained from butyl alcohol) was hydrogenated by the studied hydrogen on a copper catalyzer and the butane which was formed was then placed in a counter. The counters used a volume of gas of 41.4 cc and 428 cc with a usual pressure of 40 mm Hg and a voltage of 1,800 V, depending upon the activity of the studied gas specimens.

The first series of experiments was conducted to explain the degree of exchange of tritium with butane: $HT + C_4H_{10} \rightleftharpoons H_2 + C_4H_9T$. The results of this series are presented in Table 9.

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Table 9. Reaction $HT + C_4H_{10} \rightleftarrows H_2 + C_4H_9T$

	Catalyzer: 40% $AlCl_3$ on Carbon 120°		Catalyzer: 20% $AlCl_3$ on Al_2O_3 123°	
Butane	n-C_4H_{10}	i-C_4H_{10}	n-C_4H_{10}	i-C_4H_{10}
Activity of H_2 (impulses/min per mole$\cdot 10^{-7}$	1.0	1.0	0.76	0.81
Analysis of products				
i-C_4H_{10} (volume percent)	11.4	85.1	23.4	78.9
n-C_4H_{10} (volume percent)	88.1	12.2	74.5	17.0
Analysis of tritium				
In i-C_4H_{10} impulses/min per mole$\cdot 10^{-5}$	1.56	0.23	1.84	2.53
In n-C_4H_{10} impulses/min per mole$\cdot 10^{-5}$	0.21	0.50	0.34	5.37
Percent of activity in C_4H_{10} (from the initial activity in the hydrogen)	0.37	0.25	0.90	3.59

It is seen from this data that the isomerized product always has a higher content of tritium, and the degree of exchange is approximately proportional to the depth of the previous polymerization. The aluminum chloride which is precipitated on the aluminum oxide is characterized by a higher catalytic action in exchange than that precipitated on carbon.

In the second series of experiments the process of exchange of tritium between radioactive hydrogen chloride and butane $TCl + C_4H_{10} \rightleftarrows HCl + C_4H_9T$ was studied. Some results of this series are presented in Table 10.

Table 10. Reaction $TCl + C_4H_{10} \rightleftarrows HCl + C_4H_9T$ (catalyzer: 20 percent $AlCl_3$ on Al_2O_3)

	Temperature (in degrees C): 107	121	121	121
Butane	n-C_4H_{10}	n-C_4H_{10}	n-C_4H_{10}	i-C_4H_{10}
Activity of HCl (impulses/min per mole$\cdot 10^{-7}$	0.97	0.97	15.7	15.7
Percent HCl in the mixture with C_4H_{10}	20	2.5	20	10
Analysis of products				
i-C_4H_{10} (volume percent)	45.3	18.5	53.4	76.0
i-C_4H_{10} (volume percent)	53.5	81.5	42.5	18.3
Analysis of tritium				
In i-C_4H_{10} (impulses/min per mole$\cdot 10^{-5}$)	0*	1.29	0.39	0.23
In n-C_4H_{10} (impulses/min per mole$\cdot 10^{-5}$)	0*	0.18	0.49	0.27
Percent of activity in C_4H_{10} from the initial activity in HCl)	-	15.6	18.4	14.1

* In this test the catalyzer was used without preliminary purging.

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This data shows a considerable degree of exchange of tritium from the radioactive hydrogen chloride, which confirms the conclusions of investigators mentioned above on the necessity of the presence of hydrogen chloride in analogous reactions with aluminum chloride. A higher content of tritium appeared in the isomerized product in the previous experiments also. Of special interest is the fact that the catalyzer was prepared in a current of hydrogen chloride and therefore naturally contained considerable quantities of the latter. If such a catalyzer is used indirectly for the reaction of exchange (TCl C_4H_{10}), the exchange does not take place and the butane obtained is not radioactive (see experiment 1, Table 10). In order for the exchange reaction to take place it was necessary to purge the catalyzer beforehand with hydrogen at 121 degrees for 3 hours with a volume speed of 4 minute -1. The absorbed inactive hydrogen chloride is blown off and the surface is free for radioactive TCl. The authors consider the real catalyzer of isomerization to be the compound $HAlCl_4$, which has a low elasticity of dissociation. An exchange of tritium and isomerization of butane takes place in the formation of the compound $TAlCl_4$.

The authors have shown with special experiments on the course of isomerization in a hydrogen atmosphere that in this process there is no exchange of hydrogen with hydrogen chloride: $H_2 + TCl \rightarrow HCl + TH$, as the hydrogen is not radioactive after the reaction.

In the third series of tests the authors studied the exchange reaction $C_4H_9T + H_2 \rightleftharpoons HT + C_4H_{10}$ on the same catalyzers.

The authors thought that the exchange of tritium between butane and hydrogen could be calculated on the basis of data of the first series of tests according to the reverse reaction of exchange ($C_4H_{10} + HT$), but this was incorrect. It was made clear that the degree of exchange depends also upon the position of tritium in the butane molecule (see Table 11); if the tritium is with the secondary hydrocarbon in n-butane, the exchange will be considerably more complete than in the case where the position of the tritium is with the primary hydrocarbon. On the other hand, the tritium with the primary hydrocarbon seems to be more mobile than that with the tertiary hydrocarbon. Unfortunately these observations are not yet explained and appear very strange; the authors suggest that this is possibly connected with the specific chemistry of tritium about which there is no knowledge.

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Table 11. Reaction $C_4H_9T + H_2 \rightleftarrows HT + C_4H_{10}$ (catalyzer; 20 percent $AlCl_3$ on Al_2O_3)

	Temperature (in degrees C)			
	121	124	128	121
Butane	$n\text{-}C_4H_{10}$	$n\text{-}C_4H_{10}$	$i\text{-}C_4H_{10}$	$i\text{-}C_4H_{10}$
Position of the tritium in butane	Primary	Secondary	Primary	Tertiary
Activity of C_4 (impulses/min per mole$\cdot 10^{-7}$)	3.56	3.87	3.63	12.0
Analysis of the product:				
$i\text{-}C_4H_{10}$ (volume percent)	38.0	35.5	85.1	89.2
$n\text{-}C_4H_{10}$ (volume percent)	61.5	64.1	8.8	3.7
Analysis of tritium:				
Activity of H_2 (impulses/min per mole$\cdot 10^{-5}$)	0.15	0.51	3.43	1.52
Activity in C_4H_{10} in relation to the initial activity in C_4H_{10} (in percent)	0.043	0.132	0.95	0.127

Considering the results of the study, the authors come to the conclusion that the first series of experiments on the exchange of tritium between hydrogen and butane indicate only the progressive loosening of butane molecules in isomerization which leads to partial exchange. The data of the second series showing the very essential role of hydrogen chloride in the isomerization reaction is more interesting.

Proposing a scheme of the mechanism of the reaction, the authors present three basic conditions: (1) in the presence of hydrogen chloride and the appropriate carrier, aluminum chloride forms a compound $HAlCl_4$, analogous to the well-known addition compounds of the type $AlCl_3 \cdot NaCl$; (2) in this condition part of the molecules ($AlCl_4$), having a stabilized spherical symmetry, alleviate the weakening of the bond H—Cl; (3) the hydrogen is oriented with regard to the catalytic surface so that in catalysis it enters the sphere of the bond of hydrogen atoms of the butane molecule. Meerwein (68), Heldman (66), and others have expressed analogous notions on the formation of the complex $AlCl_4^-$ in reactions with $AlCl_3$. Fairbrother (69) studied this question using radioactive chlorine as an indicator in the Fridel-Krafts reaction.

According to these propositions the stages of the process of isomerization of butane are reduced to the following: Butane comes in contact with the mass of the catalyzer, where the hydrogen from the HCl (in combination with $AlCl_3$), designated in the diagram H_0, enters the sphere of the bond of the carbon atom (C_2) in the butane. The bond between C_1 and C_2 is weakened and partially broken so that three hydrogen atoms and two carbon atoms are found simultaneously in the sphere of the bond of C_2. At this moment a group $(AlCl_4)^-$ exists independently between the carbon atoms C_2 and C_3; in this position the group has a tendency to obtain a hydrogen atom at C_3 and thus an unsaturated state of the bond between the carbon atoms C_2 and C_3 is created so that the methyl group C_1 can either be combined with the C_3 atom, forming isobutane, or be combined with C_2, returning to the initial form of n-butane.

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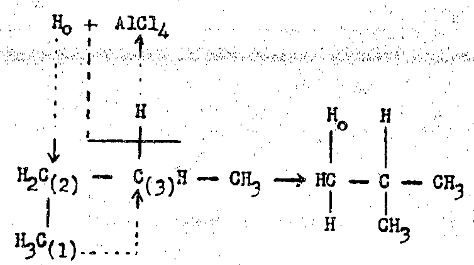

n-butane i-butane

The reverse reaction is easily explained by the same stages, but in reverse order: The isobutane comes in contact with the catalyzer so that the hydrogen atom H_0 enters the sphere of the bond of the tertiary carbon, causing a weakening and breaking of one of the bonds between the carbon atoms; at this instant the condition of the system is the same as in the third stage of the direct reaction. Thus, the formation of n- or i-butane is connected with their thermodynamic stability.

Judging from the proposed mechanism of the process, it could be expected that there must be considerable exchange of hydrogen from HCl, which was actually found in the example of the transfer of tritium from TCl to butane. On this basis it is understood why the exchange of tritium between hydrogen and butane takes place in a considerably less degree; it is possible that this exchange takes place in the beginning of the third stage of the illustrated mechanism. The authors suggest that an analogous mechanism is applicable to a number of reactions of hydrocarbons in the presence of such catalyzers as phosphoric, perchloric, and benz-sulphonic acids composed of large central groups of atoms connected with the hydrogen atoms which are directed outward.

Very similar proposals were also expressed a short time ago by B. L. Moldavskiy (67) for the reaction catalyzed by $AlCl_3$ and activated clays.

The propositions developed above make it possible to gain a new understanding of the results of the study by Brezhneva and Roginskiy (11) on the isomerization of bromic naphthalene which they obtained in 1936. These authors studied the kinetics of isomerization of alpha bromic naphthalene to beta bromic naphthalene with a catalyzer of $AlBr_3$, into the molecule of which a radioactive bromine atom had been introduced. It appeared that the speed of isomerization was much higher than the speed of exchange of bromine between $AlBr_2Br^* + (AlBr_3Br^*)R$. The bromine atoms in the sphere $(AlBr_4)$ are completely deprived of individuality and a complete exchange can be expected.

Inasmuch as absolutely dry aluminum bromide does not catalyze such reactions which need the presence of hydrogen bromide (15), then in analogy with the isomerization of butane, catalysis here is connected with the transfer of hydrogen from the beta position to the alpha position, and not with a transfer of bromine, which is only a result of the transfer of hydrogen:

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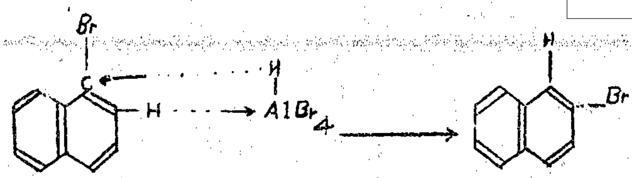

G. Isomerization of Butylene

Further development of the notion of the transfer of hydrogen by a catalyzer in the isomerization processes and a generalization of it for other analogous reactions is given in the work of Turkevich and Smith (70) in the example of the isomerization of butylene-1 and butylene-2

$$CH_2 = CH - CH_2 - CH_3 \rightleftarrows CH_3 - CH = CH - CH_3$$

with phosphoric acid as a catalyzer, using tritium as an indicator. It was found that the speed of isomerization is proportional to the pressure of the butylene and the concentration of phosphoric acid. The exchange of tritium between radioactive phosphoric acid and butylene was studied at the same time.

The speed of the exchange at 27 degrees was less than the speed of isomerization and with a specific concentration of acid, the energy of activation of the reaction was 14.5 small calories/mole, and the energy of activation of exchange was 17.8 small calories/mole. The difference in activation energies of three small calories exactly corresponds to the difference in the speeds of these processes. It can be concluded from this that both processes operate according to the same mechanism, and thus the difference in speed is due to the difference in the zero energy of the bond of hydrogen and tritium (6.253 small calories/mole for H_2 and 3.625 small calories/mole for T_2 (39)).

It was further found that radioactive water T_2O and radioactive hydrochloric acid TCl are not exchanged by tritium with butylene. On the other hand, radioactive phosphoric acid (T_3PO_4) is not exchanged with ethylene, but is exchanged with propylene.

From the observed facts, the authors offer a general theory of such catalytic reactions of hydrocarbons as cracking, isomerization, alkylation, polymerization, etc., reduced to the mechanism of a transfer of hydrogen and based on the spatial interrelationships of the catalyzer and reagent.

For example, it is supposed that the contact between the phosphoric acid and the butylene molecule takes place in the following manner: One of the hydrogen atoms of the phosphoric acid approaches the last carbon atom of butylene at the same time that an oxygen atom devoid of hydrogen approaches the third carbon atom of butylene (see diagram below); in the disintegration of this complex the phosphoric acid can carry with it the hydrogen atom from the third carbon and leave the hydrogen atom with the first carbon atom. As a result butylene-2 is formed:

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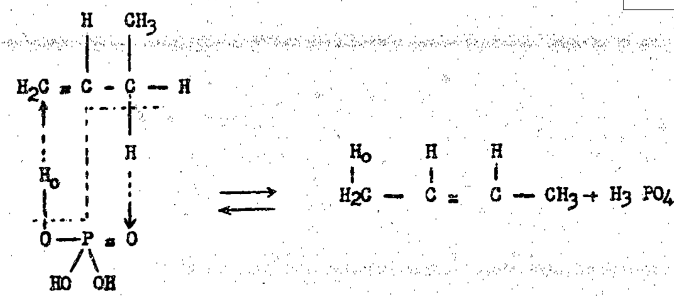
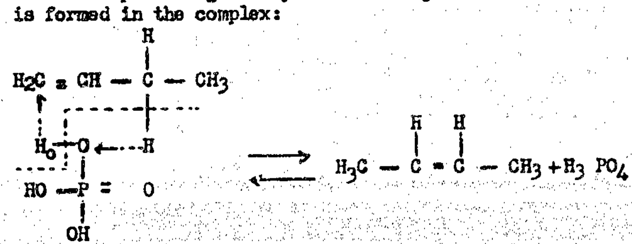


The authors maintain that this diagram closely agrees with the molecular model of butylenes and phosphoric acid.

A simpler diagram may also be imagined where a six-membered ring is formed in the complex:



The authors set forth a limiting stipulation for the catalyzer, which reduces to the fact that it must deliver and receive hydrogen atoms at a distance of approximately 3.5 Å. In their opinion, sulphuric, silicic and perchloric acids, moist $AlCl_3$ ($HAlCl_4$) and to a certain degree hydrogenated Ni fulfill this condition. However, it is not clear how these distances presented by the authors have been calculated.

According to the illustrated mechanism, the process of polymerization of hydrocarbons is like the transfer of a hydrogen atom between two olefins, the alkylation process is like a transfer of hydrogen from paraffin to olefin, the cracking process is the reverse of alkylation: the bond C — C is broken if the catalyzer (alumosilicic acid, for example) separates hydrogen from one carbon atom and transfers it to another carbon atom separated from the first.

Since all of these reactions are actually to a large extent connected with the migration of hydrogen atoms in the molecules of organic compounds, the detailed study of them using tritium as an indicator undoubtedly offers the possibility to explain the real mechanism of these processes which have great theoretical and industrial significance.

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